

Preparation, reactivities, and NMR spectra of pentafluorophenyltin derivatives[☆]

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Abstract

A variety of pentafluorophenyltin compounds were prepared and their chemical properties were examined. These compounds effectively catalyzed Mukaiyama-aldol reaction of ketene silyl acetal in sharp contrast to the inertness of normal alkyltin halides like Bu_2SnCl_2 . The increased Lewis acidity of the pentafluorophenyltin halides was proved by ^{119}Sn - and ^{13}C -NMR spectra. On the other hand, the pentafluorophenyl group reduced the reactivities of tin towards both nucleophiles and electrophiles. ^{19}F -NMR spectroscopy was invoked to elucidate this anomaly. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: NMR spectra; Pentafluorophenyltin derivatives; Mukaiyama-aldol reaction

1. Introduction

Despite their availability, alkyltin halides have seldom worked as Lewis acids in organic synthesis on account of their weak acidity [1]. We had postulated that incorporation of pentafluorophenyl groups on tin should increase the acidity. In fact, $(\text{C}_6\text{F}_5)_2\text{SnBr}_2$ proved the validity of this postulation [2]. A variety of nucleophilic reactions of silyl and stannyl reagents were effectively catalyzed by this compound under mild conditions, thus allowing otherwise difficult-to-achieve differentiations between various carbonyls or between carbonyl and acetal. The catalyst is hydrolytically stable enough to be isolated by column chromatography or recrystallization in open air. This is quite unique because most of the conventional Lewis acids that are sufficiently acidic to promote synthetically useful reactions are readily hydrolyzed. We were intrigued by these results to further expand the scope of our investigation on relevant pentafluorophenyltin compounds.

Several pentafluorophenyltin compounds are known [3–7]. Their chemical properties have also been revealed to some extent but not comprehensively. In this paper, we report the general and convenient method for preparation of various pentafluorophenyltin derivatives and their unique features that are different from normal organotin compounds. Their Lewis acidity is assessed in terms of the Mukaiyama aldol reaction. Moreover, reactions with nucleophiles and electrophiles are examined. These reactivity profiles are discussed on the basis of NMR spectra.

2. Results and discussion

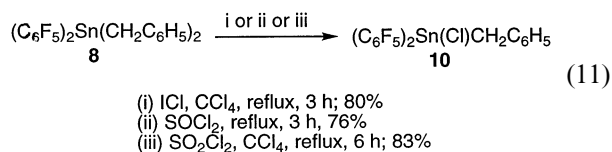
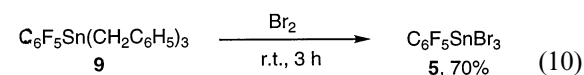
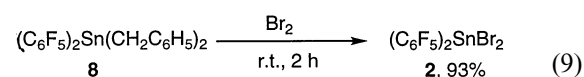
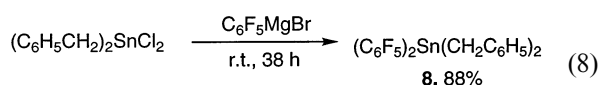
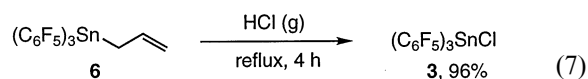
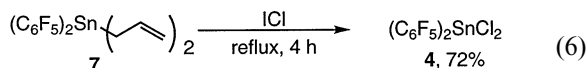
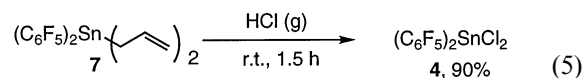
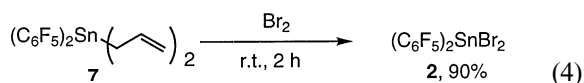
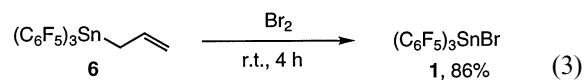
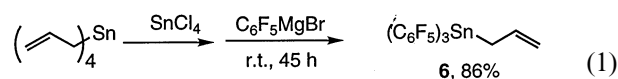
2.1. Synthesis

The precedent methods to prepare pentafluorophenyltin halides basically had recourse to treatment of SnCl_4 with $\text{C}_6\text{F}_5\text{MgBr}$ [3,4]. Quite naturally, it is not easy to obtain a single product by this procedure: usually $(\text{C}_6\text{F}_5)_3\text{SnCl}$ and $(\text{C}_6\text{F}_5)_2\text{SnCl}_2$ constitute a major fraction of the product mixture even if the stoichiometry of the Grignard reagent was adjusted to produce one of

[☆] Dedicated to the late Professor Rokuro Okawara, a pioneer of organotin chemistry.

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these halides. One exceptional method involved the selective cleavage of the *p*-tolyl group in *p*-tolyltris(pentafluorophenyl)tin to furnish $(\text{C}_6\text{F}_5)_3\text{SnCl}$ [5]. Now, we have explored more general routes to arrive at pentafluorophenyltin halides **1–5** utilizing readily cleavable allyl and benzyl groups. Allylpentafluorophenyltin derivatives **6** and **7** were produced using allyltin chlorides that could be conveniently prepared by redistribution of commercially available $(\text{CH}_2=\text{CHCH}_2)_4\text{Sn}$ and SnCl_4 [8]. Exposure of these allyltin chlorides to an excess of $\text{C}_6\text{F}_5\text{MgBr}$ [6,9] provided **6** and **7** quantitatively (Eqs. (1) and (2)). Treatment of these compounds with bromine furnished sole products $(\text{C}_6\text{F}_5)_3\text{SnBr}$ (**1**) and $(\text{C}_6\text{F}_5)_2\text{SnBr}_2$ (**2**), respectively (Eqs. (3) and (4)). Reaction of **7** with HCl gas proceeded smoothly at room temperature (r.t.) to give $(\text{C}_6\text{F}_5)_2\text{SnCl}_2$ (**4**) (Eq. (5)) while the reaction of **6** should be run at refluxing temperature in CCl_4 to give $(\text{C}_6\text{F}_5)_3\text{SnCl}$ (**3**) (Eq. (7)) (vide infra for the detailed discussion). The conversion of **7** to **4** was also effected by use of ICl though the yield was somewhat lower (Eq. (6)). Benzyltin derivatives serve as well. Thus, action of $\text{C}_6\text{F}_5\text{MgBr}$ on $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{SnCl}_2$, that is feasible from benzyl chloride and tin powder [10], led to **8** (Eq. (8)). Exposure of this compound to bromine offered another access to **2** (Eq. (9)). Notably, this route is somewhat better than the allyltin protocol (Eq. (4)) because a by-product, 1,2,3-tribromopropane forms occasionally if the amount of Br_2 deviates from the pinpoint stoichiometry. Separation of this by-product from **2** by column chromatography is rather difficult. However, the allyltin method for **1** (Eq. (3)) has no problem since 1,2,3-tribromopropane, if formed, can be readily separated from **1**. In addition, the benzyltin method was applied to produce $\text{C}_6\text{F}_5\text{SnBr}_3$ (**5**) from $\text{C}_6\text{F}_5\text{Sn}(\text{CH}_2\text{C}_6\text{H}_5)_3$ (**9**) (Eq. (10)). The requisite **9** was prepared by the Grignard reaction with tribenzyltin chloride that is also readily available from benzyl chloride and tin powder [10]. The selective cleavage of one of the benzyl groups in **8** afforded mixed triorganotin chloride **10** (Eq. (11)). The three methods employed here gave rise to virtually no difference in yield. In all of the above cases, the desired compounds were isolated solely without contamination of by-products. The compounds thus obtained are stable to hydrolysis and can be purified by column chromatography or recrystallization in open air.

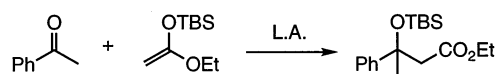


2.2. Activity as Lewis acid catalysts

The catalytic activity of pentafluorophenyltin compounds was assessed for the aldol reaction of acetophenone with ketene silyl acetal (Table 1). It is rather surprising that $(\text{C}_6\text{F}_5)_4\text{Sn}$ [6] exhibited no activity (entry 1) because a considerable degree of the acidity is expected from the estimated order of electron-withdrawing power: $\text{Cl} > \text{C}_6\text{F}_5 > \text{Br}$ [4]. Replacement of one of the C_6F_5 groups with bromine dramatically improves the activity (entry 2). The dihalides gave rise to further increase of the yield (entries 3 and 4) but a lower yield was obtained with tribromide **5**. It follows from these reactivity profiles that the catalytic activity cannot be straightforwardly associated with the electron-withdrawing power. Diallyl- and dibenzyltin derivatives **7** and **8** afforded poor yields (entries 6 and 7). Notably, both **2** and **4** are the first diorganotin dihalides that function as Lewis acids in the synthetically useful reaction. More remarkable is the effectiveness of **1** since usually triorganotin halides are not employable in organic synthesis due to the weak acidity. In this regard,

Table 1

Reaction of ketene ethyl *tert*-butyldimethylsilyl acetal with acetophenone catalyzed by pentafluorophenyltin derivatives^a



Entry	L.A.	Yield (%) ^b
1	(C ₆ F ₅) ₄ Sn	0
2	(C ₆ F ₅) ₃ SnBr (1)	71
3	(C ₆ F ₅) ₂ SnBr ₂ (2)	92
4	(C ₆ F ₅) ₂ SnCl ₂ (4)	93
5	C ₆ F ₅ SnBr ₃ (5)	77
6	(C ₆ F ₅) ₂ Sn(CH ₂ CH=CH ₂) ₂ (7)	10
7	(C ₆ F ₅) ₂ Sn(CH ₂ C ₆ H ₅) ₂ (8)	4

^a Reaction conditions; ketone:ketene silyl acetal:L.A. was 1.0:1.3:0.1, CH₂Cl₂, –78°C, 4 h.

^b Isolated yield.

we conclude that the C₆F₅ group is effective for increasing the Lewis acidity but, unfortunately, not so powerful as chlorine and bromine.

To get further insight into this aspect, the interactions between the organotin halides with carbonyls were probed by ¹¹⁹Sn- and ¹³C-NMR (Table 2) [11]. Upon addition of five equivalents of acetophenone or propanal, the ¹¹⁹Sn signal of **2** experienced appreciable upfield shifts [Δδ (¹¹⁹Sn)] which reflected the increase in coordination number of tin. On the other hand, much smaller variations were observed with Bu₂SnCl₂ that was catalytically inactive for the aldol reaction. The variation of ¹³C chemical shifts of the carbonyl carbon [Δδ (¹³C)] is in accord with the ¹¹⁹Sn-NMR. The δ values moved downfield appreciably upon mixing with **2** whereas only slight or virtually no change was induced with Bu₂SnCl₂. Obviously, the pentafluorophenyltin compound undergoes stronger coordination than Bu₂SnCl₂ indicative of the increase in

the acceptor property by incorporation of the C₆F₅ groups.

2.3. Reactivity

There appeared several reports which referred to the reactivities of pentafluorophenyltin derivatives [4–7]. These studies, however, were focused mostly on elucidation of the characteristics of the Sn–C₆F₅ bond itself. We disclose herein that the C₆F₅ group exerts significant influences on the reactivities of other residues attached on tin. As shown in Eq. (12), pentafluorophenyltin bromides **1** and **2** underwent no reaction with NaOMe. This stands in sharp contrast to normal organotin halides that are readily converted to the methoxides under the same reaction conditions. Analogously, no reaction occurred with sodium *N,N*-diethyldithiocarbamate (Eq. (13)). The replacement of the bromines in **2** with nucleophiles was achievable only when silver salts were employed. Thus, dithiocarbamate **11** could be obtained by use of silver *N,N*-diethyldithiocarbamate (Eq. (14)). The C₆F₅ group also suppressed the nucleophilic attack by Grignard and organozinc reagents. Reaction with C₆H₅MgBr was monitored by TLC and the reactivity was qualitatively assessed in terms of the reaction temperature and time required for disappearance of the pentafluorophenyltin halides [12]. It turned out that the reactivity increases with the decrease in the number of the C₆F₅ group: **1** < **2** < **5** (Eqs. (15) (16) and (17)). A similar trend holds in the reaction with Et₂Zn (Eqs. (18) (19) and (20)). Apparently, the reactivity of **1** and **2** towards nucleophiles is low in spite of the strong acidity of tin compared to normal organotin halides.

In addition to the above nucleophilic reactions, the pentafluorophenyltin compounds are also reluctant to undergo electrophilic attacks. As described already, the tin–allyl bond in **7** was readily cleaved by HCl gas at r.t. (Eq. (5)). Under the same conditions no reaction took place with **6** and the refluxing temperature in

Table 2

Organotin/carbonyl interaction studied by ¹¹⁹Sn- and ¹³C-NMR spectra^a

	δ (¹¹⁹ Sn)	Δδ (¹¹⁹ Sn) ^b	δ (¹³ C) ^c	Δδ (¹³ C) ^b
(C ₆ F ₅) ₂ SnBr ₂ (2)	–236			
Bu ₂ SnCl ₂	127			
PhCOMe			197.6	
C ₂ H ₅ CHO			202.7	
(C ₆ F ₅) ₂ SnBr ₂ (1.0) + PhCOMe (5.0)	–358	–122	198.4	0.8
(C ₆ F ₅) ₂ SnBr ₂ (1.0) + C ₂ H ₅ CHO (5.0)	–356	–120	204.6	1.9
Bu ₂ SnCl ₂ (1.0) + PhCOMe (5.0)	85	–42	197.7	0.1
Bu ₂ SnCl ₂ (1.0) + C ₂ H ₅ CHO (5.0)	74	–53	203.2	0.5

^a In dry CH₂Cl₂ with Me₄Sn and Me₄Si as internal standards at r.t.

^b Change of chemical shifts upon coordination.

^c The chemical shift of carbonyl carbon.

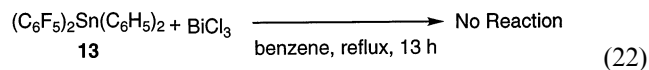
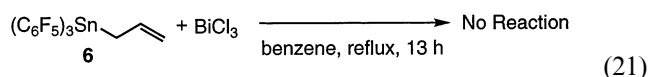
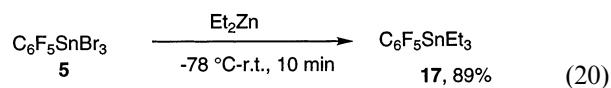
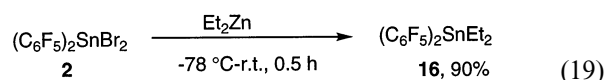
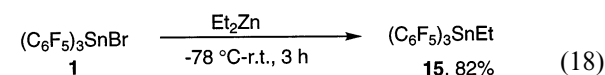
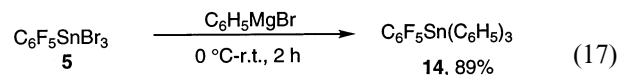
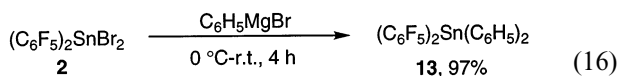
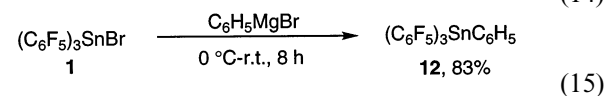
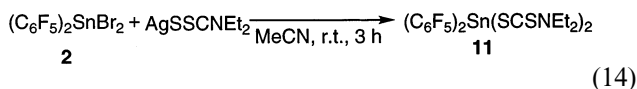
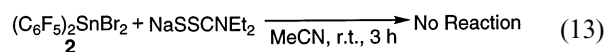
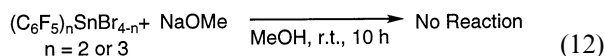
Table 3
 ^{19}F -NMR spectra of pentafluorotin compounds^a

	δ_p ($\Delta\delta$) ^b	δ_m ($\Delta\delta$) ^b	δ_o ($\Delta\delta$) ^b
$(\text{C}_6\text{F}_5)_4\text{Sn}$	−82.4	−93.8	−57.6
$(\text{C}_6\text{F}_5)_3\text{SnBr}$ (1)	−81.4 (1.0)	−93.5 (0.3)	−57.2 (0.4)
$(\text{C}_6\text{F}_5)_2\text{SnBr}_2$ (2)	−80.7 (1.7)	−93.4 (0.4)	−58.3 (−0.7)
$(\text{C}_6\text{F}_5)_3\text{SnCl}$ (3)	−81.4 (1.0)	−93.5 (0.3)	−57.8 (−0.2)
$(\text{C}_6\text{F}_5)_2\text{SnCl}_2$ (4)	−80.6 (1.8)	−93.4 (0.4)	−58.4 (−0.8)
$(\text{C}_6\text{F}_5)_3\text{SnCH}_2\text{CH}=\text{CH}_2$ (6)	−84.1 (−1.7)	−94.6 (−0.8)	−57.2 (0.4)
$(\text{C}_6\text{F}_5)_2\text{Sn}(\text{CH}_2\text{CH}=\text{CH}_2)_2$ (7)	−85.8 (−3.4)	−95.3 (−1.5)	−57.1 (0.5)
$(\text{C}_6\text{F}_5)_2\text{Sn}(\text{CH}_2\text{C}_6\text{H}_5)_2$ (8)	−86.0 (−3.6)	−95.6 (−1.8)	−56.8 (0.8)
$\text{C}_6\text{F}_5\text{Sn}(\text{CH}_2\text{C}_6\text{H}_5)_3$ (9)	−87.3 (−4.9)	−96.0 (−2.2)	−56.2 (1.4)
$(\text{C}_6\text{F}_5)_2\text{Sn}(\text{C}_6\text{H}_5)_2$ (13)	−85.5 (−3.1)	−95.1 (−1.3)	−55.7 (1.9)
$(\text{C}_6\text{F}_5)_2\text{Sn}(\text{SSCNEt}_2)_2$ (11)	−91.2 (−8.8)	−97.6 (−3.8)	−64.3 (−6.7)
$(\text{C}_6\text{F}_5)_2\text{Sn}(\text{Cl})\text{CH}_2\text{C}_6\text{H}_5$ (10)	−83.4 (−1.0)	−94.7 (−0.9)	−57.8 (−0.2)

^a In dry CH_2Cl_2 with $\text{CF}_3\text{C}_6\text{H}_5$ as an internal standard at r.t.

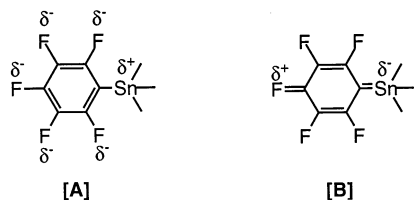
^b The difference from that of $(\text{C}_6\text{F}_5)_4\text{Sn}$ is given in the parentheses.

CCl_4 was required for the effective conversion (Eq. (7)). The reactivity decreased as the number of C_6F_5 group was increased as was the case in the nucleophilic reactions. The reduced reactivity of **6** is rather surprising because allyl–tin bond usually undergoes the facile cleavage [13]. The reluctance was also observed in the reaction of **6** with BiCl_3 (Eq. (21)). This contrasts with our finding that $\text{Bu}_2\text{Sn}(\text{CH}_2\text{CH}=\text{CH}_2)_2$ was readily converted to Bu_2SnCl_2 on treatment with BiCl_3 in benzene at r.t. Deactivation by the C_6F_5 groups was not restricted to the tin–allyl bond but the tin–phenyl bond also was not cleaved by BiCl_3 in refluxing benzene (Eq. (22)) while Bu_2SnPh_2 was converted smoothly to Bu_2SnCl_2 under the same reaction conditions [14].



2.4. ^{19}F -NMR

With a view to obtain information about the unusual reactivities of pentafluorophenyltin compounds, ^{19}F -NMR spectroscopy was invoked. It is accepted that the chemical shift (δ_p) of *p*-fluorine in the C_6F_5 group is sensitive to the mesomeric effect and thus diagnostic for the perturbation of the electronic states [15,16]. In Table 3 these values for various pentafluorophenyltin derivatives are given along with those of the *ortho*- (δ_o) and *meta*-fluorine (δ_m) chemical shifts. The $\Delta\delta$ values given in parentheses represent the deviations from the corresponding chemical shifts of $(\text{C}_6\text{F}_5)_4\text{Sn}$. Apparently, $\Delta\delta_p$ are larger than $\Delta\delta_o$ and $\Delta\delta_m$ [5]. The replacement of one or two C_6F_5 groups in $(\text{C}_6\text{F}_5)_4\text{Sn}$ by halogen(s) gave rise to downfield shifts of the δ_p values (positive $\Delta\delta$ values) while upfield shifts (negative $\Delta\delta$ values) resulted from the substitution by the organic groups. These outcomes are accounted for in terms of the difference in the conflicting resonance structures shown below. In general, the increase in the Lewis acidity of pentafluorophenyltin compounds unambiguously reflects the major contribution of structure A.



However, the electron-withdrawing halogens increases the contribution of B, resulting in the downfield shift of δ_p compared to that of $(C_6F_5)_4Sn$ whereas the electron-donating organic groups have the opposite effect. The superiority of pentafluorophenyltin halides to $(C_6F_5)_4Sn$ in the catalytic activity suggests that the polarization by A does not play a primary role for increasing the acidity as compared with the electron withdrawal by halogens. This electron-withdrawing power, furthermore, overwhelms the partial electron return induced by B, thus serving for enhancement of the catalytic activity. The failure of the nucleophilic displacement of bromine in **1** and **2** (Eqs. (12) and (13)) and the decreasing reactivity towards organometallic reagents with increasing number of the C_6F_5 groups (Eqs. (15) (16) (17) (18) (19) and (20)) would also be accommodated in this notion. The mesomeric effect could counterbalance, to some extent, the affinity of tin for nucleophiles that is induced by the innate electron-withdrawing character of the C_6F_5 group. The reluctance to the electrophilic attack, on the other hand, cannot be interpreted straightforwardly. Obviously, the relatively large upfield shifts of δ (^{19}F) of **6** indicate the transfer of electron from the allyl group to the C_6F_5 group consistent with the decrease of reactivity. However, if such simple interpretation is valid, allyltin chlorides should also suffer from the analogous but stronger effect due to the higher electronegativity of chlorine than the C_6F_5 group. However, this compound, in fact, underwent the facile cleavage of the allyl group by $BiCl_3$ under the same conditions. As a whole, the reactivities of pentafluorophenyltin derivatives are governed by the delicate balance of the polarity and mesomeric effects.

3. Experimental section

All reactions were performed under argon atmosphere. THF and diethyl ether were distilled from sodium benzophenone ketyl and dichloromethane was distilled from calcium hydride prior to use. CCl_4 was distilled from P_2O_5 and stored over molecular sieves 4A before use. Dibenzyltin dichloride and tribenzyltin chloride were prepared according to literature procedure [10]. Melting points were not corrected. 1H - and ^{13}C -NMR were recorded on Bruker-400 and Varian Gemini-300 spectrometers in $CDCl_3$ with Me_4Si as an internal standard. ^{119}Sn - and ^{19}F -NMR were recorded

on Bruker-400 spectrometer with internal Me_4Sn and trifluoromethylbenzene standards, respectively. Mass spectra were obtained with a JEOL JMS-700 mass spectrometer. Elemental analyses were performed with a Perkin Elmer 2400 CHN instrument.

3.1. $(C_6F_5)_3SnCH_2CH=CH_2$ (**6**)

To an ether solution (100 ml) of tetraallyltin (0.71 g, 2.5 mmol) was added tin chloride (1.95 g, 7.5 mmol) at $-50^\circ C$. The mixture was warmed to $0^\circ C$ in 30 min. Then, a Grignard solution in ether (50 ml) (prepared from Mg turnings (0.96 g, 40 mmol) and C_6F_5Br (9.34 g, 38 mmol)) was added dropwise at $0^\circ C$. After being stirred at r.t. for 45 h, the mixture was filtered on a celite pad and quickly passed through a short silica gel column (hexane). The filtrate was evaporated and the residue was purified by column chromatography on silica gel (hexane) to give **6** (5.67 g, 86%) m.p. $65^\circ C$. 1H -NMR δ 2.85 (d, 2H, $J = 8.2$ Hz, $J_{Sn-H} = 92$ Hz), 4.94 (d, 1H, $J = 10.0$ Hz), 5.07 (d, 1H, $J = 16.9$ Hz), 5.84–5.99 (m, 1H); ^{119}Sn -NMR: δ -153.7 ; ^{19}F -NMR δ -57.2 , -84.1 , -94.6 ; MS (m/z) 662(M^+); Anal. calc. for $C_{21}H_5F_{15}Sn$: C, 38.16; H, 0.76; Found C 38.12, H 1.12.

3.2. $(C_6F_5)_2Sn(CH_2CH=CH_2)_2$ (**7**)

To an ether solution (100 ml) of tetraallyltin (2.12 g, 7.5 mmol) was added tin chloride (1.95 g, 7.5 mmol) at $-50^\circ C$. The mixture was warmed to $0^\circ C$ in 30 min. Then, a Grignard solution in ether (50 ml) (prepared from Mg turnings (0.91 g, 38 mmol) and C_6F_5Br (8.61 g, 35 mmol)) was added at $0^\circ C$. After being stirred at r.t. for 75 h, the mixture was filtered on a pad celite and quickly passed through a silica gel column (hexane). The filtrate was evaporated and the residue was purified by column chromatography on silica gel (hexane) to give **7** (7.9 g, 98%). 1H -NMR δ 2.58 (d, 4H, $J = 8.2$ Hz, $J_{Sn-H} = 81$ Hz), 4.89 (d, 2H, $J = 10.3$ Hz), 5.02 (d, 2H, $J = 18.1$ Hz), 5.86–6.03 (m, 2H); ^{119}Sn NMR δ -101.6 ; ^{19}F -NMR δ -57.1 , -85.8 , -95.3 ; MS (m/z) 536(M^+); Anal. calc. for $C_{18}H_{10}F_{10}Sn$: C, 40.41; H, 1.88; Found C, 40.62; H, 1.84.

3.3. $(C_6F_5)_3SnBr$ (**1**) [4]

To a dry CCl_4 solution (30 ml) of $(C_6F_5)_3SnCH_2CH=CH_2$ (5.67 g, 8.6 mmol) was added dropwise bromine (1.36 g, 8.6 mmol) at $0^\circ C$. The mixture was stirred at r.t. for 3 h and evaporated. The resulting yellow oil was purified by column chromatography (hexane followed by benzene) to give **1** (5.13 g, 86%); m.p. 108 – $110^\circ C$; lit. m.p. 107 – $108^\circ C$; ^{119}Sn -NMR δ -198.3 ; MS (m/z) 700 (M^+).

3.4. $(C_6F_5)_2SnBr_2$ (**2**) [4]

To a dry CCl_4 solution (20 ml) of $(C_6F_5)_2Sn(CH_2CH=CH_2)_2$ (1.50 g, 2.80 mmol) was added dropwise bromine (0.89 g, 5.60 mmol) at $0^\circ C$. The mixture was stirred at r.t. for 1 h and evaporated. The resulting yellow oil was purified by column chromatography (hexane followed by benzene) to give **2** (1.54 g, 90%); ^{119}Sn -NMR δ –236.5; MS (m/z): 612 (M^+); Anal. calc. for $C_{12}Br_2F_{10}Sn$: C, 23.53; found C: 23.47.

To a dry CCl_4 solution (30 ml) of $(C_6F_5)_2Sn(CH_2C_6H_5)_2$ (2.5 g, 3.94 mmol) was added dropwise bromine (1.25 g, 7.88 mmol) at $0^\circ C$. The mixture was stirred at r.t. for 2 h and evaporated. The resulting yellow oil was purified by column chromatography (hexane followed by benzene) to give **2** (2.22 g, 93%).

3.5. $(C_6F_5)_2SnCl_2$ (**4**) [4]

Into a dry CCl_4 solution (30 ml) of $(C_6F_5)_2Sn(CH_2CH=CH_2)_2$ (1.07 g, 2.0 mmol) was bubbled dry hydrogen chloride gas at r.t. for 1.5 h. After removal of the solvent, the residual oil was purified by column chromatography (hexane followed by benzene) to give **4** (0.94 g, 90%); ^{119}Sn -NMR δ –88.9; MS (m/z): 526 (M^+).

A dry CCl_4 solution (30 ml) of $(C_6F_5)_2Sn(CH_2CH=CH_2)_2$ (2.11 g, 4.0 mmol) and ICl (1.41 g, 8.0 mmol) was heated under reflux for 4 h. After removal of the solvent, the residual oil was purified by column chromatography (hexane followed by benzene) to give **4** (1.50 g, 72%).

3.6. $(C_6F_5)_3SnCl$ (**3**) [5]

Into a refluxing CCl_4 solution (50 ml) of $(C_6F_5)_3SnCH_2CH=CH_2$ (4.54 g, 6.88 mmol) was bubbled dry hydrogen chloride gas for 4 h. After removal of the solvent, the crude product was recrystallized from petroleum ether (b.p. $< 50^\circ C$) to give **3** (4.34 g, 96%); m.p. 108 – $110^\circ C$, lit. m.p. 108 – $109^\circ C$; ^{119}Sn -NMR δ –123.9; MS (m/z): 656 (M^+).

3.7. $(C_6F_5)_2Sn(CH_2C_6H_5)_2$ (**8**)

To a suspension of Mg turnings (0.72 g, 30 mmol) in dry ether (50 ml) was added an ether solution (15 ml) of C_6F_5Br (6.15 g, 25 mmol) at $0^\circ C$. The mixture was stirred for 2 h. A THF solution (15 ml) of dibenzyltin dichloride (3.70 g, 10 mmol) was added dropwise at $0^\circ C$. After being stirred at r.t. for 38 h, the mixture was filtered on a celite pad and quickly passed through a short silica gel column (hexane). The filtrate was evaporated and the residue was purified by column chromatography on silica gel (hexane) to give **8** (5.55 g, 88%); m.p. 67 – $68^\circ C$; 1H -NMR: δ 3.06 (s, 4H, J_{Sn-H} =

74 Hz), 6.93–7.18 (m, 10 H); ^{119}Sn -NMR δ –102.0; ^{19}F -NMR: δ –56.8, –86.0, –95.6; MS (m/z): 636 (M^+); Anal. calc. for $C_{26}H_{14}F_{10}Sn$, C, 49.17, H, 2.22. Found C, 48.98, H, 2.16.

3.8. $C_6F_5Sn(CH_2C_6H_5)_3$ (**9**)

To a suspension of Mg turnings (168 mg, 7 mmol) in dry ether (10 ml) was added an ether solution (5 ml) of C_6F_5Br (1.48 g, 6 mmol) at $0^\circ C$. The mixture was stirred for 2 h. A THF solution (10 ml) of tribenzyltin chloride (2.13 g, 5 mmol) was added dropwise at $0^\circ C$. After being stirred at r.t. for 63 h, the mixture was filtered on a celite pad and quickly passed through a short silica gel column (hexane). The filtrate was evaporated and the residue was purified by column chromatography on silica gel (hexane) to give **9** (2.70 g, 97%); m.p. 51 – $52^\circ C$; 1H -NMR: δ 2.60 (s, 6H, J_{Sn-H} = 67 Hz), 6.76–7.18 (m, 15 H); ^{119}Sn -NMR δ –63.2; ^{19}F -NMR δ –56.2, –87.3, –96.0; MS (m/z): 560 (M^+); Anal. calc. for $C_{27}H_{21}F_5Sn$: C, 58.00; H, 3.79; Found C, 57.85, H, 3.71.

3.9. $C_6F_5SnBr_3$ (**5**)

To a dry CCl_4 solution (30 ml) of $C_6F_5Sn(CH_2C_6H_5)_2$ (1.51 g, 2.7 mmol) was added dropwise bromine (1.28 g, 8.1 mmol) at $0^\circ C$. The mixture was stirred at r.t. for 3 h and evaporated. The residue was purified by column chromatography (hexane followed by benzene) to give **5** (0.98 g, 70%); ^{119}Sn -NMR δ –289.4; ^{19}F -NMR δ –57.8, –81.4, –93.5; MS (m/z): 524 (M^+); HRMS calc. for $C_6Br_3F_5Sn$ 523.6494, found 523.6509.

3.10. $(C_6F_5)_2Sn(Cl)CH_2C_6H_5$ (**10**)

To a dry CCl_4 solution (30 ml) of $(C_6F_5)_2Sn(CH_2C_6H_5)_2$ (1.0 g, 1.58 mmol) was added ICl (563 mg, 3.48 mmol) at r.t. The mixture was heated under reflux for 3 h and evaporated. The residue was purified by column chromatography (hexane followed by benzene) to give **10** (0.73 g, 80%); ^{119}Sn -NMR δ –96.6; ^{19}F -NMR δ –58.2, –80.2, –93.1; MS (m/z): 580 (M^+); HRMS calc. for $C_{19}H_7ClF_{10}Sn$ 579.9098, found 579.9099.

$(C_6F_5)_2Sn(CH_2C_6H_5)_2$ (1.0 g, 1.58 mmol) and $SOCl_2$ (1.63 g, 13.8 mmol) was mixed at $0^\circ C$. The mixture was heated under reflux for 3 h and evaporated. The residue was purified by column chromatography (hexane followed by benzene) to give **10** (0.69 g, 76%).

To a dry CCl_4 solution (30 ml) of $(C_6F_5)_2Sn(CH_2C_6H_5)_2$ (1.0 g, 1.58 mmol) was added SO_2Cl_2 (1.68 g, 12.5 mmol) at $0^\circ C$. The mixture was heated under reflux for 6 h and evaporated. The resulting yellow oil was purified by column chromatography (hexane followed by benzene) to give **10** (0.76 g, 83%).

3.11. $(C_6F_5)_2Sn(SCSNEt_2)_2$ (**11**)

To an acetonitrile solution (10 ml) of $(C_6F_5)_2SnBr_2$ (610 mg, 1 mmol) was added $Et_2NCSSAg$ (512 mg, 2 mmol) at r.t. The solution was stirred for 1 h and then evaporated. Benzene was added and the mixture was filtered to remove $AgBr$. The benzene was evaporated and the crude product was recrystallized from dichloromethane–hexane to give **11** (607 mg, 81%): 1H -NMR δ 1.31 (t, 12 H, $J = 7.1$ Hz), 3.71 (q, 8 H, $J = 7.1$ Hz); ^{119}Sn -NMR δ –540.2; ^{119}F -NMR δ –64.2, –91.2, –97.5; MS (m/z): 750 (M^+); Anal. calc. for $C_{22}H_{20}F_{10}N_2S_4Sn$: C, 35.26, H, 2.69, N, 3.74 found C, 35.45, H, 2.64, N, 3.24.

3.12. $(C_6F_5)_3SnC_6H_5$ (**12**) [5]

To an ether solution (3 ml) of $(C_6F_5)_3SnBr$ (209 mg, 0.3 mmol) was added Grignard reagent C_6H_5MgBr (prepared from Mg turnings (9.6 mg, 0.4 mmol) and C_6H_5Br (57 mg, 0.36 mmol) in dry ether (3 ml)) at $0^\circ C$. The reaction mixture was stirred for 8 h. Then, the mixture was filtered on a celite pad and quickly passed through a short silica gel column (hexane) to give **12** (192 mg, 83%): m.p. 95 – $96^\circ C$, lit. m.p. 95 – $96^\circ C$; ^{119}Sn -NMR δ –186.9; MS (m/z): 698 (M^+).

3.13. $(C_6F_5)_2Sn(C_6H_5)_2$ (**13**) [5]

To an ether solution (3 ml) of $(C_6F_5)_2SnBr_2$ (306 mg, 0.5 mmol) was added Grignard reagent C_6H_5MgBr (prepared from Mg turnings (36 mg, 1.5 mmol) and C_6H_5Br (220 mg, 1.4 mmol) in dry ether (3 ml)) at $0^\circ C$. The reaction mixture was stirred for 4 h. Then, the mixture was filtered on a celite pad and quickly passed through a short silica gel column (hexane) to give **13** (295 mg, 97%): m.p. 84 – $85^\circ C$, lit. m.p. $85^\circ C$; ^{119}Sn -NMR δ –158.2; MS (m/z): 608 (M^+).

3.14. $C_6F_5Sn(C_6H_5)_3$ (**14**) [5]

To an ether solution (3 ml) of $C_6F_5SnBr_3$ (209 mg, 0.4 mmol) was added Grignard reagent C_6H_5MgBr (prepared from Mg turnings (43 mg, 1.8 mmol) and C_6H_5Br (251 mg, 1.6 mmol) in dry ether (3 ml)) at $0^\circ C$. The reaction mixture was stirred for 2 h. Then, the mixture was filtered on a celite pad and quickly passed through a short silica gel column (hexane) to give **14** (184 mg, 89%): m.p. 84 – $85^\circ C$, lit. m.p. $86^\circ C$; ^{119}Sn -NMR δ –139.3; MS (m/z): 518 (M^+).

3.15. $(C_6F_5)_3SnEt$ (**15**) [7]

To a CH_2Cl_2 solution (3 ml) of $(C_6F_5)_3SnBr$ (209 mg, 0.3 mmol) was added Et_2Zn (0.15 ml 1 M solution in hexane, 0.15 mmol) at $-78^\circ C$. The reaction mixture

was stirred at r.t. for 3 h and subjected to column chromatography on silica gel (hexane) to give **15** (178 mg, 82%): m.p. 98 – $99^\circ C$; 1H -NMR δ 1.39 (t, 3H, $J = 7.9$ Hz), 2.03 (q, 2H, $J = 7.9$ Hz, $J_{Sn-H} = 67$ Hz); ^{119}Sn -NMR δ –136.3; MS (m/z): 650 (M^+).

To an ether solution (5 ml) of $(C_6F_5)_3SnBr$ (209 mg, 0.3 mmol) was added a Grignard reagent in ether (5 ml) (prepared from Mg (10.6 mg, 0.44 mmol) and $EtBr$ (43.6 mg, 0.4 mmol)) at $0^\circ C$. After being stirred at r.t. for 7 h, the mixture was subjected to column chromatography on silica gel (hexane) to give **15** (175 mg, 81%).

3.16. $(C_6F_5)_2SnEt_2$ (**16**) [7]

To a CH_2Cl_2 solution (3 ml) of $(C_6F_5)_2SnBr_2$ (245 mg, 0.4 mmol) was added Et_2Zn (0.40 ml 1 M solution in hexane, 0.40 mmol) at $-78^\circ C$. The reaction mixture was stirred for 0.5 h and was subjected to column chromatography on silica gel (hexane) to give **16** (183 mg, 90%): ^{119}Sn -NMR δ –61.5; MS (m/z): 512 (M^+).

3.17. $C_6F_5SnEt_3$ (**17**) [7]

To an ether solution (3 ml) of $C_6F_5SnBr_3$ (200 mg, 0.38 mmol) was added Et_2Zn (0.57 ml 1 M solution in hexane, 0.57 mmol) at $-78^\circ C$. The reaction mixture was stirred for 10 min at $-78^\circ C$ and was subjected to column chromatography on silica gel (hexane) to give **17** (114 mg, 80%): ^{119}Sn -NMR δ –6.8. MS (m/z): 374 (M^+).

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